Study on PVDF Ultrafiltration Membrane Experiment Preparation and Membrane Formation Mechanism

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Abstract. This paper explores the impact of solution copolymerization of hydrophobic monomer (MMA and VAc) and hydrophilic monomer (AA and MAA) on casting membrane solution and PVDF membrane. Through experimental results and representations, it shows that, with NVP content proportion in monomer decreases, the viscosity of casting membrane solution decreases and it is in the form of instantaneous demixing in the pure water coagulation bath (except for Ml), with the average effective aperture distribution widens and MWCO increase; with NVP content proportion in monomer decreases, the viscosity of casting membrane solution and light transmission rate increases first and then decreases; membrane fracture surface structure exists in the form of large-scale finger hole; porosity, membrane flux and average effective aperture all increase first and then decrease, exerting relatively high reject rate on PEG series.

1. Introduction

Membrane separation technique is a burgeoning efficient isolation technique, which has been internationally recognized as one of the most prominent high-tech production technologies [1 - 2]; ultrafiltration membrane technique is a kind of membrane separation technique started in 1960s-1970s, and its fundamental principle is to make use of fenestra selective screening property to separate, abstract and condense matter, which has been widely applied in fields of wastewater treatment, medicine, food, chemistry, environmental protection, and so on. PVDF is a kind of high polymer material with good chemical resistance, high-temperature resistance, oxidative resistance, and weather resistance, and it cannot be eroded by acid, alkali, strong oxidant, or halogen; at the same time, it is high-intensive and its safety performance meets the requirements of American NSF standards. All of these advantages make PVDF as preferred ultrafiltration membrane material. There are mainly two methods to produce PVDF ultrafiltration membrane: conversion method of immersion and precipitation, and thermally induced phase separation (TIPS) ［3］. But, as a kind of organic polymer material, PVDF has low surface energy and high hydrophobicity; sole PVDF homopolymer cannot produce ultrafiltration membrane with proper water flux and small aperture. During recent years, scholars have made a large amount of research on PVDF modification from two aspects of blending modification and graft modification.

To enhance the hydropilia of PVDF untrafiltration membrane and increase its anti-pollution capacity in water treatment, this paper adopts phase inversion to prepare blending modification ultrafiltration membrane of inorganic nanoparticles and PVDF. Through FTIR representing copolymer, light transmission rate and viscosity, this paper analyzes casting film solution features, and analyzes the impact of copolymer on PVDF membrane through such representation methods as SEM, pure water flux, interception, contact angle and mechanical property.

2. Experiment preparation

2.1 Experiment material

The main medicine in the experiment: PVDF (Suwei (Shanghai) Co. ltd), N,N- DMAc(China Shanghai Xiangyang Chemical Reagent Company), N- NVP(China Jiaozuo Zhongwei Chemical Industry), and so on. The experimental facilities include constant temperature magnetic stirrer,

precision electric mixer, digital constant temperature water bath pot, TOC, SEM, fourier infrared spectrometer, and so on from Shanghai Siyue Instrument Company.

2.2 Preparation and characterization of PVDF membrane

This paper uses free radical solution polymerization to synthesize copolymer, with AIBN as thermal initiator. Resolve monomer ration (6 wt%) into DMAc(73.5 wt%), and add AIBN (occupies 8 wt% of the monomer content); after uniform dissolution, put it in the thermostat water bath of 80 ° C to make mechanical agitation for 6h, so as to gain solution of copolymer. Make dialysis and purification of copolymer solution with the dialysis bag of 1000 Da-molecular-cutoff, with purewater as external solution; after 2-day dialysis, the DMAc solution can be fully replaced. Put the solution after dialysis in the 60 X vacuum drying oven to make it dry. Make purification with dialysis bag, and make FTIR analysis of dried copolymer; test copolymer can be tested with FT 1600 fourier infrared spectrometer.

Place PVDF powder in the oven of 60 ° C for more than 24h, to make it intensively dry. Put quantitative PVDF polymer (20 wt%) into the polymer solution produced in 2.2.2 slowly; put the solution in thermostat water bath of 60 ° C to dissolve 2h; stop stirring, make it standing and defoam it, till uniform casting film solution is got.
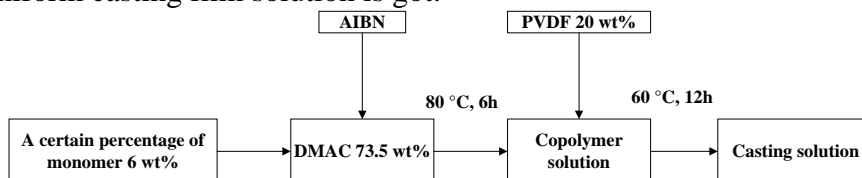

Figure1 Configuring membrane liquid flow chart

Take 300 mg/L of polyethylene glycol solutions with different molecular weights (PEG 2000, 4000, 6000, 10000 and 20000) as trapped fluid to circulate the whole equipment; make prepressing for 30 min under the pressure of 0.1 Mpa; use total organic carbon analyzer (TOC) to measure the concentration of polyethylene glycol mother solution and membrane permeate.

The pure water flux and reject rate of PVDF membrane can be got through (1) and (2):

$$J_W = Q / A \times t \qquad （1）$$

$$R = \frac{C_f - C_p}{C_f} \times 100\% \qquad （2）$$

In the formula, Jiv: pure water flux (:L/(m2*hX);Q: transit dose of pure water (L);A: available membrane area (m2);t: penetration time (h);R: reject rate ;C_f: concentration of trapped fuild stoste (mg/L);C_p: concentration of membrane permeate(mg/L)。

Porosity is measured through dry and wet quality law. Cut a piece of even wet membrane, wipe the water drops on the membrane with filter paper, weigh the wet weight; put the membrane in the oven of 60 ° C to dry for 3h; weight the dry wight. The formula for porosity:

$$\varepsilon = \frac{(m_1 - m_2)\rho_w}{(m_1 - m_2)\rho_w + m_2\rho_p} \times 100\% \qquad （3）$$

In the formula, porosity m1: weight of wet membrane (g); m2: weith of dry membrane (g); ρ w density of water(0.998 g • cm^3); Pp: density of PVDF (1.780 g • cm^3).

Use electronic universal testing machine QJ-2014 to measure the mechanical property of dry PVDF membrane after immersing in glycerinum water (strength of extension, elongation at break and elasticity modulus). At room temperature, set sample overall length 40 mm, width 5 mm, measured spacing 25 m, extension rate 50 mm/min, and the maximum tension is 50 N. Every sample should be tested at least 5 times to get the average value.

3. Analysis of impact on membrane formation of PVDF ultrafiltration improvement

3.1 NVP and hydrophobic monomers impact on PVDF membrane

Hydrophobic monomer chooses MMA and VAc respectively. NVP monomer has an acyl with strong polar, which means it is hydrophilic monomer; but the methylene on the backbone of MMA and the methyl perssad on the side chain are hydrophobic, the copolymerization of these two monomers can easily prepare reactive polymer with surface activity. This paper studies the impact of copolymers of P(NVP-co-MMA) and P(NVP-co-VAc) on the function of membrane, fixes the total content of PVDF and two comonomers, and change the mole ratio of two monomers; the specific matching can be seen in Table 1.

Table 1: Constitution table of membrane M1-M10 casting membrane solution

No.	Mol ratio of monomer	Total monomer	PVDF(wt%)	DMAc(wt%)	AIBN(wt%)
Ml	8NVP: 2MMA	6	20	73.5	0.5
M2	7NVP: 3MMA	6	20	73.5	0.5
M3	5NVP: 5MMA	6	20	73.5	0.5
M4	3NVP: 7MMA	6	20	73.5	0.5
M5	2NVP: 8MMA	6	20	73.5	0.5
M6	8NVP: 2VAc	6	20	73.5	0.5
M7	7NVP: 3VAc	6	20	73.5	0.5
M8	5NVP: 5VAc	6	20	73.5	0.5
M9	3NVP: 7VAc	6	20	73.5	0.5
MIO	2NVP: 8VAc	6	20	73.5	0.5

Put small amount of product into the dialysis bag with molecular cutoff of 1000, and make dialysis in pure water; after 2 days of dialysis, put it in vacuum drying oven of 60 ° C to dry it. The synthesis of copolymer of P(NVP-co-VAc) is the same as that of P(NVP-co-MMA).

Figure 2 and 3 show the gelation rate of casting membrane solution in water after P(NVP-co-MMA) and P(NVP-co-VAc) blend with PVDF. From Figure 2, we can see that NVP:MMA is 8:2; the light transmission coefficient decreases from 1.0 rapidly to 0.05 or so (the time take is 70s), and keeps stable at about 0.05. It means that after casting membrane solution is immersed into gelation bath, the gelation curing phenomenon is obvious and membrane is produced rapidly; the exchange rate between DMAc and pure water gelation bath is very fast and the elation process is instantaneous demixing. The structure of membrane formed in instantaneous demixing can be observed by SEM, and even the specific part such as membrane shape can be discussed. When NVP:MMA is 8:2, light transmission coefficient decreases slowly, and keeps stable at 0.6 at last. It is because that the mole ratio of NVP and MMA is 8:2, and the synthetic copolymer slows the gelation rate of casting membrane solution; the gelation process is delay demixing.

In Figure 3, we can see that NVP:VAc is 5:5; all the other casting membrane solution systems are instantaneous demixing; in the membrane structure, intensified surface with large holes is easily to form145]; the membrane shape can be observed. When NVP:VAcis 5:5, there is delay demixing and the light transmission coefficient keeps stable at about 0.05. The mechanism is similar to P(NVP-co-MMA) blending with PVDF; when the ratios of two hydrophobic monomers polymerizing with NVP are the same, the light transmission change laws in casting membrane

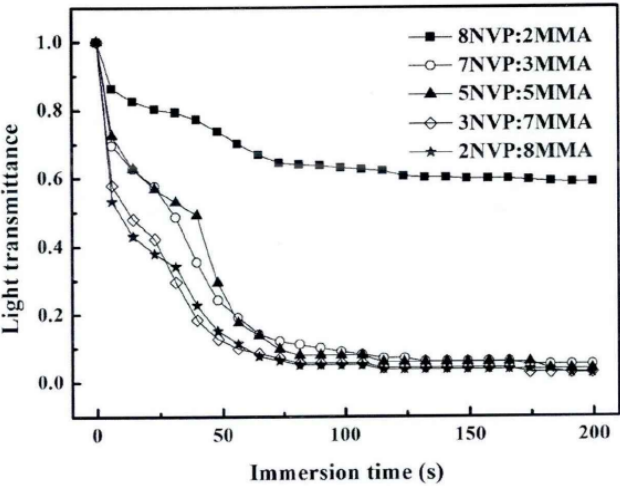solution systems are totally different, which is mainly influenced by the features of poly(vinyl acetate.

Figure 2 Gelation rate figure of PVDF/DMAc/P(NVP-co-]VIIVlA) system casting membrane solution in water
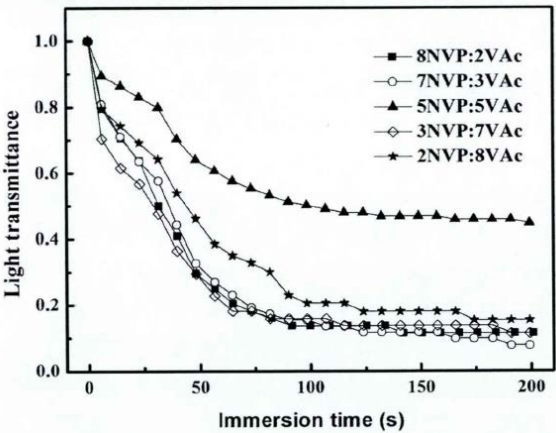

Figure 3 PVDF / DMAc / P (NVP-co-VAc) system gel casting solution in water rate chart

Figure 4 and 5 are the pore diameter distribution curve and probability density function of copolymers of P(NVP-co-MMA) and P(NVP-co-VAc) modified PVDF membrane
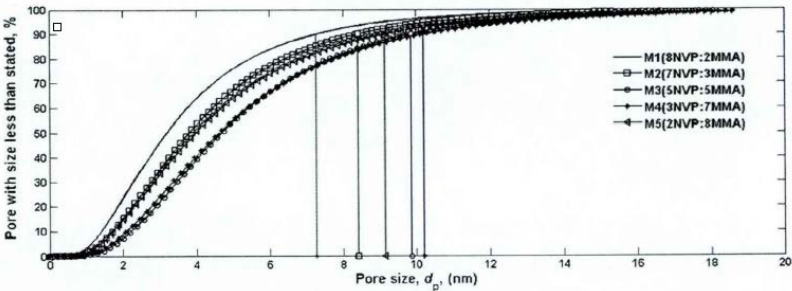

Figure 4 Pore diameter distribution curve and probability density function of P(NVP-co-MMA) modified PVDF membrane
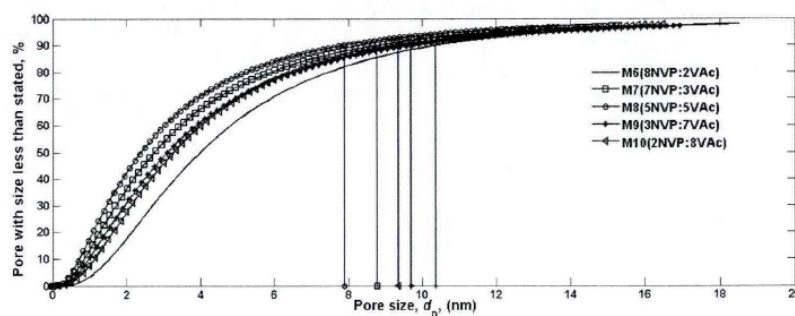
Figure 5 Pore diameter distribution curve and probability density function of P(NVP-co-VAc) modified PVDF membrane

It can be seen that with the portion of NVP content in copolymer decreases, except for M5, the average effective aperture distribution of PVDF/P(NVP-co-MMA) membrane becomes wide and MWCO increases. With the portion of NVP content in copolymer decreases, the pore diameter distribution of PVDF/P(NVP-co-VAc) membrane changes in accordance with the flux; the average effective aperture distribution becomes narrow first and then wide; MWCO increases first and then decreases.

3.2 The effect of copolymerization of NVP and hydrophilic monomer on PVDF

The mixing of copolymers of NVP and hydrophilic monomers of AA and Maa, and PVDF base material, have effect on the properties of casting membrane solution and membrane; the specific matching can be seen in Table 2.

Table 2 Constitution table of casting membrane solution of membrane M11-M18

No.	Monomer mol ratio	Total monomer	PVDF(wt%)	DMAc(wt%)	AIBN(wt%)
M11	9NVP: lAA	6	20	73.5	0.5
M12	8NVP: 2AA	6	20	73.5	0,5
M13	7NVP: 3AA	6	20	73.5	0.5
M14	6NVP: 4AA	6	20	73.5	0.5
M15	9NVP: IMA A	6	20	73.5	0.5
M16	8NVP: 2MAA	6	20	73.5	0.5
Ml7	7NVP: 3MAA	6	20	73.5	0.5
M18	6NVP: 4MAA	6	20	73.5	0,5

Figure 6 and 7 are the gelation rate drawings of P(NVP-co-AA) and P(NVP-co-MAA) modified PVDF membrane system casting membrane solution. From Figure 6, we can see that when NVP:AA is 9:1, casting membrane solution has instantaneous demixing; afterwards, NVP:AA is 8:2, the process is delay demixing; when NVP:AA is 7:3 or the content of AA is larger, the gelation rate increases to the maximum and then decreases gradually. As the proportion of AA increases, casting membrane solution exits in the milk white state; when it is immersed in gelation bath, the light transmission coefficient is small; with the prolongation of gelation time, it presents transparent state, when the light transmission efficient is the largest; as the gelation time prolongs further, the membrane gelation solidifies and the light transmission coefficient decreases rapidly.

From Figure 7, we can see that when the monomer ratio in P(NVP-co-MAA), NVP:MAA, is 9:1, casting membrane solution has delay demixing; then with the proportion of MAA in comonomer increases, the casting membrane solution has instantaneous demixing. The light transmission coefficient of membrane M16 and M17 keeps stable at 0.1 or so, and the time needed is only 50s;

but the gelation rate of membrane M18 is relatively slow in 0-75 s; after 75s, the membrane light transmission decreases rapidly. There are many reasons leading to the randomness of gelation rate: the first is that with the increase of MAA content, casting membrane solution color changes from transparency to milk white, which interferes gelation rate; the second is that the change of MAA proportion in copolymer P(NVP-co-MAA) changes the stability of casting membrane solution, which causes the changes in gelation rate.
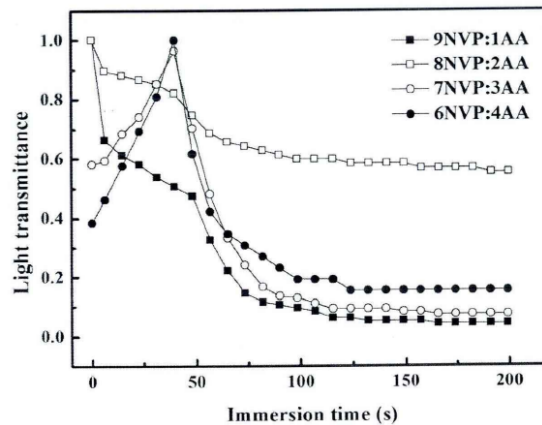

Figure 6: Gelation rate of PVDF/DMAc/P(NVP-co-AA)system casting membrane solution in water
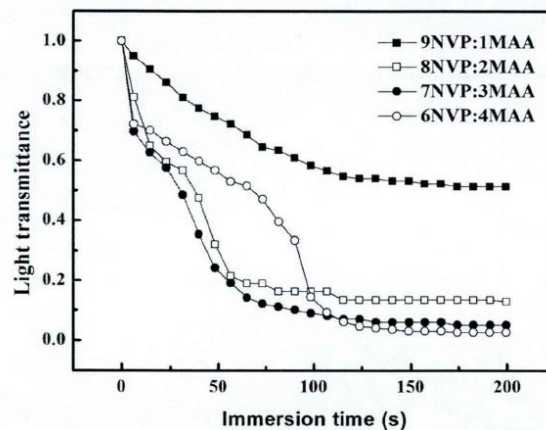

Figure7: Gelation rate of PVDF/DMAc/P(NVP-co-MAA) system casting membrane solution in water

Figure 8 and 9 are the pore diameter distribution curve and probability density function of copolymers of P(NVP-co-AA) and P(NVP-co-MAA) modified PVDF membrane. From Figure 2.27, it can be seen that with AA proportion increases in copolymer, the average effective aperture of PVDF/P(NVP-co-AA) membrane is 2.18-3.63 nm, which decreases and the increases; MWCO keeps stable and the growing rate is not obvious. This is in accordance with the increase of PAA content, the increase of microsmic apertures in membrane and the increase of aperture diameter. The small flux gets tight membrane surface, and H and MWCO are small; the large flux gets compact membrane fracture surface with apertures on it, and ^l and MWCO become large. The pore diameter distributions of NVP and hydrophilic monomer copolymerization modified membrane and hydrophobic monomer modified membrane are not the same; the membrane with large flux has wider average effective aperture.
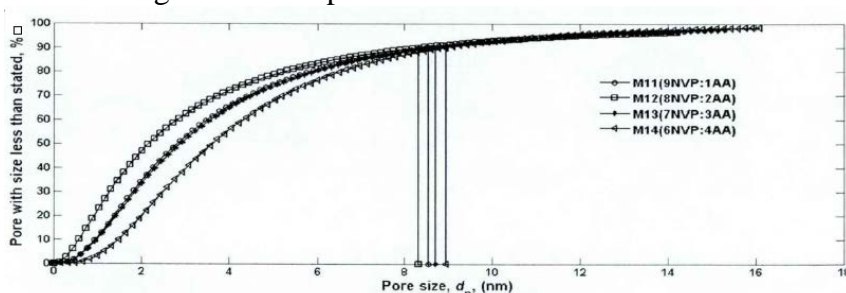
Figure 8: Pore diameter distribution curve and probability density function of P(NVP-co-AA) modified PVDF membrane
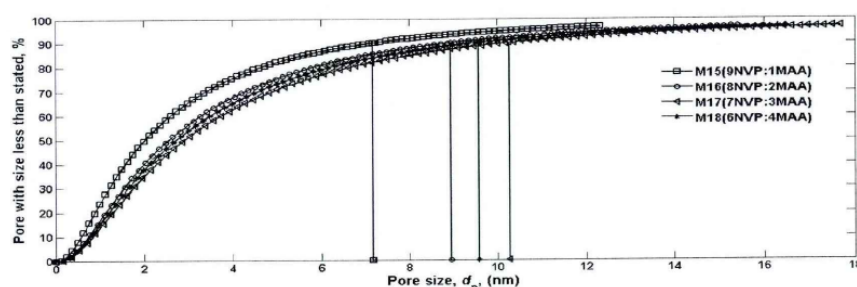

Figure 9: Pore diameter distribution curve and probability density function of P(NVP-co-MAA) modified PVDF membrane

4 Conclusions

PVDF has properties of anti-pollution , chemical stability, radiation characteristic and heat resistance, which is the perfect high polymer material to make ultrafiltration membrane. Blending modification and surface modification methods are the main means to elevate the hydrophilia, anti-pollution and mechnical strength of PVDF ultrafiltration membrane. This paper discusses the influence of the copolymerization of NVP and hydrophobic monomer (MMA and VAc) and hydrophilic monomer (AA and MAA) on casting membrane solution and PVDF membrane respectively, and concludes that with the decrease of NVP proportion in monomer, the viscosity of casting membrane solution decreases and has instantaneous demixing in pure water gelation bath (except for Ml); the structure of membrane fracture surface has large finger-shape holes and the porosity decreases progressively. With the decrease of NVP proportion in monomer, casting membrane solution velocity and light transmission rate increases first and then decreases; the structure of membrane fracture surface also has large finger-shape holes; porosity, membrane flux and average effective aperture all increase first and then decrease, and have rather high reject rate on PEG series.

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